

Heat Conduction in κ -(BEDT-TTF)₂Cu(NCS)₂

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The first study of thermal conductivity, κ , in a quasi-two-dimensional organic superconductor of the κ -(BEDT-TTF)₂X family reveals features analogous to those already observed in the cuprates. The onset of superconductivity is associated with a sudden increase in κ which can be suppressed by the application of a moderate magnetic field. At low temperatures, a finite linear term - due to a residual electronic contribution- was resolved. The magnitude of this term is close to what is predicted by the theory of transport in unconventional superconductors.

The superconductors of κ -(BEDT-TTF)₂X family [1] share a number of similarities with the high- T_c cuprates [2]. Both sets of compounds are quasi-two-dimensional with superconductivity confined to conducting planes sandwiched between insulating layers. The metallic state in both families exhibit common features like low carrier densities, strong electronic correlations and proximity of antiferromagnetic insulating state. While Shubnikov-de Haas experiments [3] have established the existence of a well-defined Fermi surface in the κ -(BEDT-TTF)₂X family, this metallic state presents some more unconventional properties - like a pseudogap in the electronic density of states in κ -(BEDT-TTF)₂Cu[N(CN)₂]Br [4]- which have been compared to analogous features in underdoped cuprates [2]. As for the symmetry of the superconducting order parameter, it has yet to become the subject of a consensus as nowadays it is the case in the cuprates. While, early penetration-depth studies on κ -(BEDT-TTF)₂Cu(NCS)₂ led to conflicting results [5], recent NMR [6] and specific heat [7] studies on κ -(BEDT-TTF)₂Cu[N(CN)₂]Br provided evidence for the presence of nodes in the superconducting gap.

In this letter we present the first study of thermal conductivity in a member of this family. According to our results, heat transport in κ -(BEDT-TTF)₂Cu(NCS)₂ presents features which have already been detected in YBCO and other high- T_c cuprates. Notably, the observation of a residual electronic thermal conductivity at very low temperatures provides strong support for presence of nodes in the superconducting order parameter.

We measured the thermal conductivity of five κ -(BEDT-TTF)₂Cu(NCS)₂ single crystals using a conventional four-probe method. Contacts were realized using silver paint on evaporated gold. The heat current was always applied in the basal (highly-conducting) plane. The temperature gradient was measured with two RuO₂ resistance chips which showed small magnetoresistance and a usable sensitivity up to 15K. The resistive heater and the two thermometers were held by small solenoids of 50 μ m manganin wire. In this way, we measured the resistance of the sample and the thermometers with

minimal heat loss. For temperatures below 0.25 K, we checked our zero-field results by using another device which was designed for very low temperatures and described elsewhere [8]. Our set-up allowed us to measure, in addition to electrical and thermal conductivities, the thermo-electric power of the sample. Direct visual measurements of sample dimensions led to a gross determination of the geometric factor ($\pm 50\%$) due to irregularities in samples' shape and thickness. Determining the absolute value of the resistivity proved to be very difficult. We found room temperature resistivities varying from 35 to 80 m Ω cm. A comparable dispersion can be found in the technical literature on this compound. We used a unique room-temperature-resistivity value (54 m Ω cm) when comparing different samples. At very low temperatures, we found that in all samples the voltage signal of the standard IVVI configuration was less than the IIVV one (the order of Is and Vs refer to the spatial sequence of current(I) and voltage(V) electrodes on the sample). This is a signature of a meandering charge current path characteristic of highly-anisotropic superconductors with inhomogenous contacts [9]. Therefore, we refrained to use the nominal value of resistivity in our analysis of thermal conductivity data.

Fig. 1 presents the effect of the superconducting transition on the temperature dependence of the thermal conductivity. We present the results for the two samples which were most thoroughly studied. The striking feature of the figure is the upturn in thermal conductivity at the onset of the superconducting transition. All the samples studied presented such an upturn, but its intensity -reflected in the height of the consequent peak in $\kappa(T)$ - was found to be strongly sample-dependent. The ratio $\frac{\kappa_{max}}{\kappa(T_c)}$ is 1.3 in sample #1 and 1.05 in sample #2. We observed a ratio as high as 2.7 in one sample which was quickly deteriorated after a thermal cycle. This strong variation suggests that heat conduction is much sensitive to a type of disorder which affects only mildly the electrical resistivity. The residual restivity ratio $\frac{\rho(300K)}{\rho(T \rightarrow 0)}$ is 410 in sample #1 and 250 in sample #2. The positive sign of

thermopower for both samples indicated that the orientation of heat current was nearly parallel to the quasi-one-dimensional sheets of Fermi surface and thus mainly implying the hole-like carriers of the two-dimensional pockets [10].

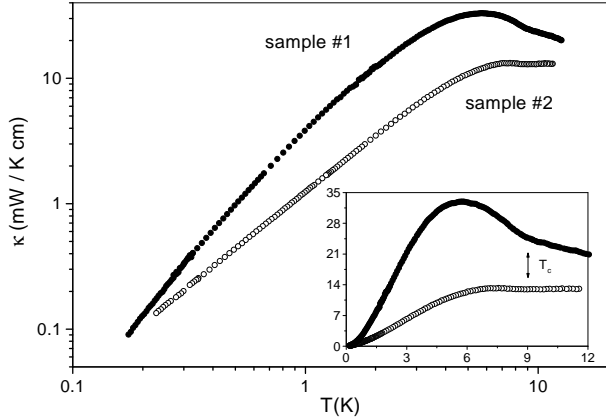


FIG. 1. Temperature dependence thermal conductivity in two different samples. Note the upturn at T_c . Inset shows a linear presentation.

A similar upturn in the thermal conductivity of high- T_c superconductors has been a subject of controversy for several years [11]. The increase in thermal conductivity below T_c indicates that the condensation of electrons in the superconducting state strengthens heat transport by reducing the scattering of heat carriers. The debate was centered on the identity of these heat carriers. While an orthodox scenario [12] invoked an increase in the lattice conductivity due to condensation of electrons, experimental evidence for a very unusual increase in the electronic relaxation time in the superconducting state [13] led to the suggestion [11] that at least part of the upturn in κ is due to a steep increase in the electronic contribution. Strong support for the latter point of view was provided by thermal Hall effect measurements [14]. In the case of κ -(BEDT-TTF) $_2$ Cu(NCS) $_2$, the origin of the upturn raises the same questions. Surface resistance studies have reported an increase in the microwave conductivity of the system below T_c [15]. Compared to YBCO [13] this increase is modest, but its very existence makes it tempting to stretch the analogy with the cuprates and suggest that part of the upturn in $\kappa(T)$ reported here is due to electrons. However, the Wiedemann-Franz law (with should be employed very cautiously due to the uncertainties on the absolute value of resistivity) implies that just above T_c , the electronic contribution counts for only 5% of the total thermal conductivity. Thus, while the final issue of the question shall wait for thermal Hall effect measurements in the superconducting state of this compound, one can safely attribute the main part of this feature to the enhancement in the lattice conductivity

consequent to a sudden decrease in electronic scattering at T_c . This very visible effect of electronic condensation on lattice conductivity indicates the strength of the electron-phonon coupling in this system as already documented by neutron diffraction [16] and Raman scattering [17] studies. This is to be contrasted to the case of (TMTSF) $_2$ ClO $_4$, where lattice conductivity was found to remain unchanged by the superconducting transition [8].

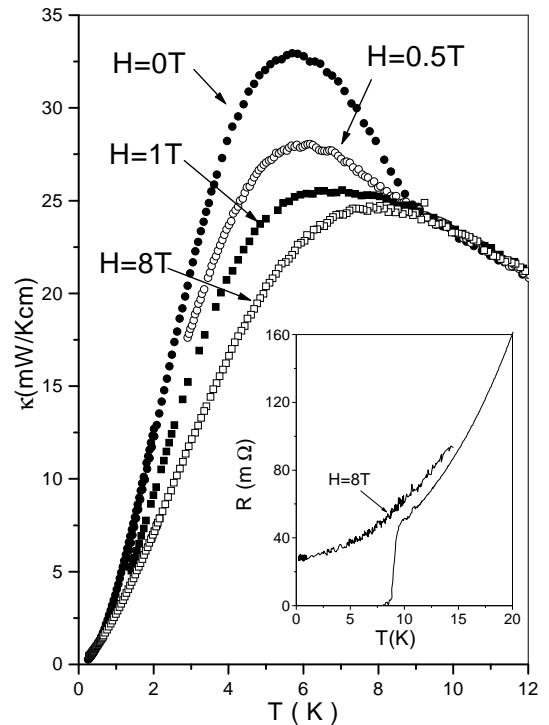


FIG. 2. The temperature dependence of the thermal conductivity in sample#1 for different fields. Inset shows the temperature dependence of the resistance of the same sample.

A supplementary source of information is the effect of the magnetic field. Figure 2 shows $\kappa(T)$ of sample#1 for different values of magnetic field. The inset of the figure shows the electrical resistivity of the normal and the superconducting states. In the normal state, a magnetic field of 8T does not affect the thermal conductivity within the experimental resolution ($\approx 1\%$), but it induces a sizeable (15 %) decrease in charge conductivity. This is an additional indication of lattice-dominated thermal conductivity in the vicinity of T_c .

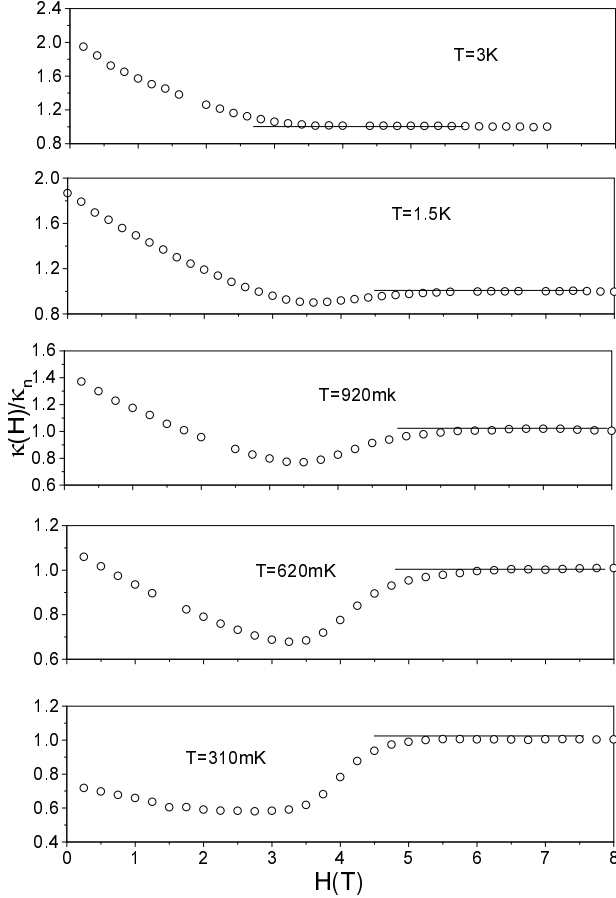


FIG. 3. The field dependence of the normalized thermal conductivity in sample #1 for different temperatures. Deviation from the horizontal line marks H_{c2} . Note the gradual apparition of a dip at low temperatures.

The peak is suppressed with the application of a moderate magnetic field. But the decrease in thermal conductivity is only monotonous at higher temperatures. This is seen in fig. 3 which presents the field-dependence of thermal conductivity for various temperatures. To reduce undesired effects associated with vortex pinning, the sample was cooled in the normal state (i.e. in a field greater than H_{c2}) to the corresponding temperature and then κ was measured as a function of decreasing field. For temperatures higher than 2K, thermal conductivity decreases with increasing field as a result of the reintroduction of the scattering quasi-particles by the magnetic field. A more remarkable structure reminiscent of the heavy-fermion superconductor URu_2Si_2 [19]- appears at lower temperatures when $\kappa(H)$ exhibits a dip. This minimum indicates a competition between increasing and decreasing contributions to κ . Note that only the electronic component can be enhanced by the application of a magnetic field. Thus, the size of the jump in $\kappa(H)$ just below H_{c2} is an upper limit to the difference between

electronic thermal conductivities in the normal and superconducting states. According to an early theory [18], in the vicinity of H_{c2} , the fading of a spatially inhomogeneous gap leads to a rapid enhancement in the density of states of quasi-particles travelling perpendicular to the vortex axes. The slope of $\kappa(H)$ at H_{c2} is related to the topological details of the superconducting gap.

The main part of the initial field-induced decrease of thermal conductivity is due to the effect of the magnetic field on the phonon mean-free-path. However, an estimation of the dominant phonon wavelength at low temperatures ($\lambda_{ph} = \frac{\hbar v_s}{k_B T} \simeq 240nm/K$) exceeds by two order of magnitudes the coherence length at $T=0.62K$ so that no vortex scattering of phonons is expected. This is confirmed by the regular decrease in $\kappa(H)$ up to fields of a few teslas. The vortex scattering of heat carriers has been reported in much smaller fields with long intervortex distances [20]. Here, the observed field-induced decrease is a result of the scattering of phonons by electronic excitations including those which are extended out of the vortex cores. As first pointed out by Volovik [21], the enhancement of these latter delocalized electronic excitations by a magnetic field due to a doppler shift in quasi-particle spectrum dominates the properties of the mixed state of unconventional superconductors [22].

Evidence for unconventional superconductivity comes from our low-temperature results. Fig. 4 presents the low-temperature behaviour of thermal conductivity in normal and superconducting states for samples #1 and #2. The remarkable feature of the figure is the presence of a finite linear term in the thermal conductivity of the superconducting state indicative of a residual electronic contribution. In both samples the magnitude of this term is a sizeable fraction of the normal electronic term. For sample #1, we extended our zero-field measurements down to $T=0.16K$ and found that for $T \leq 0.27K$, $\kappa(T)$ presents a $aT + bT^3$ temperature dependence with $a = \kappa_e^s/T \pm 0.09mW/K^2cm$ and $b = 11 \pm 5mW/K^4cm$. The large uncertainties are mainly due to the geometric factor. The cubic term gives an estimation of the maximum phonon mean-free-path using the kinetics gaz equation $\kappa_{ph} = \frac{1}{3}c_{ph}v_sl_{ph}$, where $c_{ph} = \beta T^3$ is the lattice specific heat ($\beta = 23.6\mu J/K^4cm^3$ [23]) and v_s the velocity of sound ($v_s = 5.10^3m/s$ [24]). This yields $l_{ph} = 28\mu m$ which is comparable to the sample thickness ($\simeq 20\mu m$). In the normal state, due to the lack of data for $T \leq 0.25K$ the extraction of κ_e^n/T value at $T=0$ is less straightforward. But one can reasonably expect that the ballistic regime (with a phonon mean-free-path comparable to sample dimensions) should be attained at a similar temperature range. Moreover, the magnitude of the cubic term (which depends on phonon thermodynamics and sample geometry) should be identical in the normal and superconducting states. In this way, the zero-temperature κ_e^n/T can be estimated to be $0.95mW/K^2cm$. As expected, the difference between the electronic thermal conductivities of the normal and

superconducting states is comparable with the jump in $\kappa(H)/T$ just below H_{c2} at $T = 0.31$ K, which- as argued above- is exclusively electronic and gives an estimate of $\kappa_e^n - \kappa_e^s$. In the case of sample #2, due to the lack of low-temperature data, the analysis remains qualitative.

The theory of heat transport in unconventional superconductors predicts a finite zero-temperature value for $\frac{\kappa_s}{T}$ due to impurity scattering of residual quasi-particles [25]. Moreover, for certain gap topologies- including the one associated with the $d_{x^2-y^2}$ symmetry- the magnitude of this linear term is universal at small concentrations of impurity: $\frac{\kappa_{00}}{T} = \frac{\hbar k_b^2 \omega_p^2}{6e^2 S}$, where ω_p is the plasma frequency and $S = \frac{d\Delta_0}{d\Phi}$ is the slope of the gap at the node. The experimental validity of this theory has been recently reported in the case of $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ [26]. In our case, using $\hbar\omega_p \simeq 0.6 \pm 0.1 \text{ eV}$ [27] and $2\Delta_0 = 4.8 \pm 1.1 \text{ meV}$ [28] and assuming a standard d-wave gap with $S = 2\Delta_0$ one expects $\frac{\kappa_{00}}{T} = 0.16 \pm 0.05 \text{ mW/K}^2\text{cm}$ in very good agreement with the experimental result.

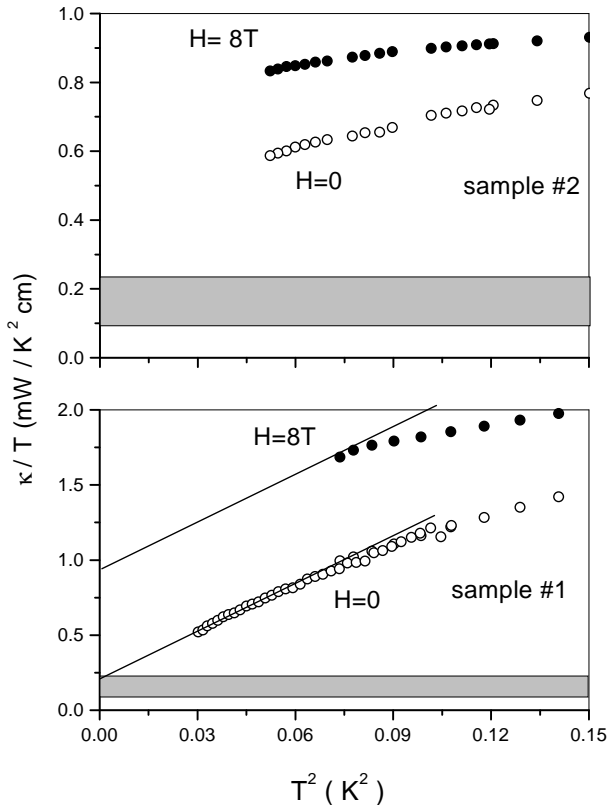


FIG. 4. The T^2 dependence of κ/T in normal and superconducting states for sample #1 and sample #2. The straight lines schematize the expected $aT + bT^3$ behavior. The shaded area represents the universal linear term in the clean limit.

It is important to note that this theory has been worked out for clean superconductors with the electronic relaxation time, τ , exceeding $\frac{\hbar}{\pi\Delta_0}$. An alternative formulation of its basic statement is that the ratio of electronic conductivities in the superconducting and normal states should extrapolate to $\frac{\hbar}{\pi\tau\Delta_0} = \frac{\xi_0}{l_e}$. Compared to YBCO, $\kappa\text{-(BEDT-TTF)}_2\text{Cu(NCS)}_2$ is a rather dirty superconductor. Its electronic mean-free-path, l_e , can be estimated either using the magnitude of the threshold field for apparition of quantum oscillations (8 T) [3] or through the values of normal state conductivity (κ_e^n/T) and ω_p . Both methods yield comparable values for l_e ($\simeq 35 \text{ nm}$). The coherence length ξ_0 can be deduced from the slope of H_{c2} at T_c ($\simeq 5 \text{ nm}$). Thus the value of $\frac{\kappa_s}{\kappa_e^n}$ should extrapolate to 0.15 ± 0.05 . According to theory, this value should increase with increasing scattering rate [29], so that for dirtier samples higher ratios are expected. Fig. 4 is compatible with both of these statements. While for sample #1 we have a remarkable quantitative agreement with the theory, the extrapolated ratio in sample #2 tends to be higher. This is the first verification of the theory of transport in unconventional superconductors by directly comparing the conductivities of normal and superconducting states.

In conclusion, our study of heat conductivity in $\kappa\text{-(BEDT-TTF)}_2\text{Cu(NCS)}_2$ provides evidence for nodes in the superconducting gap, strong electron-phonon coupling and possibly an enhancement of quasi-particle scattering time below T_c . We thank H. Aubin, L. Taillefer, M. Ribault, C. Pasquier, D. Jérôme and L. Fruchter for stimulating discussions, P. Batail for his support and L. Bouvot for technical assistance.

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